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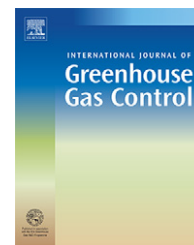
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Structure and activity relationships for amine based CO₂ absorbents—I

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ABSTRACT

A study to determine the structure and activity relationships of various amine based CO₂ absorbents was performed in which, the absorption of pure CO₂ at atmospheric pressure was measured to assess the total absorption rate and capacities. Results showed that an increase in chain length between the amine and different functional groups in the absorbent structure, result in a decrease of absorption rate whereas, the absorption capacity was increased in most absorbents.

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1. Introduction

Although the absorption of acid gases such as CO₂ in aqueous amine solutions like, e.g. MEA (monoethanolamine) from natural gas concerns proven technology, the removal of CO₂ from flue gases is not as straightforward as expected. In these oxygen containing systems problems such as degradation, precipitation, corrosion, foaming, etc., affect the process more substantially. Furthermore, in the currently used systems a major part of the operational cost is caused by the solvent regeneration (up to 40%). Therefore, exists a need to develop novel solvent systems for the removal of carbon dioxide from flue gases.

Clearly, relationships exist between the amine structure and the activity and capacity for CO₂ absorption. According to Chakraborty et al. (1986) the introduction of substituents at the α -carbon creates a carbamate instability, which causes the hydrolysis to go faster, thus increasing the amount of

bicarbonate, allowing for higher CO₂ loadings. Sartori and Savage (1983) suggested this instability was due to the steric hindrance created by these α -substituents. Chakraborty et al. (1988) examined the electronic effects of such substituents and proposed that substitution at the carbon atom results in an interaction of the π and π^* methyl group orbital with the lone pair of the nitrogen. This interaction reduces the charge at the nitrogen, resulting in a softer base, which again results in a weakening of the N–H bond. These effects allow an increase of the hydrolysis by the hydroxide (hard base) in the solution. The steric hindrance would be expected to slow the rate of the initial reaction with CO₂ to some extent, but as 1 mol of amine is released upon hydrolysis of the carbamate, the level of amine available for reaction with CO₂ increases.

To obtain a better understanding of the structure–activity relationship, solvent screening experiments are performed. The effects variables that were investigated, e.g. the chain length, increase in number of functional groups, side chain at

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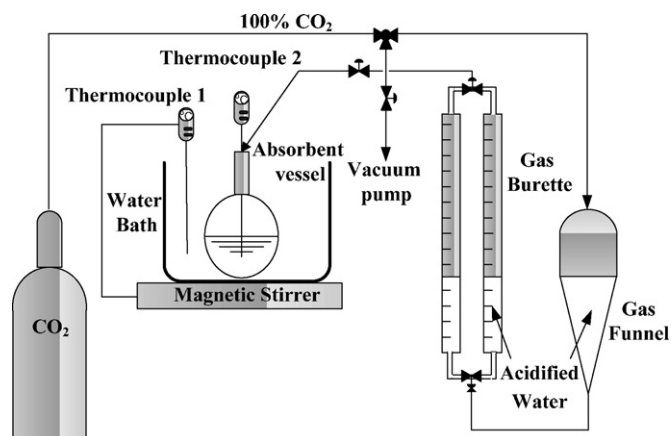


Fig. 1 – Schematic diagram of the experimental set-up for determining the absorption capacity of various amine based absorbents.

α -carbon position, alkyl group position in cyclic amine and side chain effect on cyclic amine with different functional groups, etc. A semi-quantitative representation of these effects on the initial rate of absorption for CO_2 is described, as well as the capacity of various solvents for CO_2 absorption.

2. Experiment

The various amine based absorbents were tested in a screening apparatus (see Fig. 1), where the relative rates of absorption and absorption capacity can be measured and compared to the MEA default case. The apparatus is designed to operate at atmospheric pressure and temperature up to 40°C . Before starting the experiment the absorbent sample in absorbent vessel is degassed for approximate 1 h. The temperature of the water bath was maintained at $30 \pm 0.5^\circ\text{C}$. The carbon dioxide absorption was measured by following the volume changes of pure CO_2 in gas burette over 10 ml sample of an aqueous amine solution of 2.5–0.1 mol/l, stirred at a constant rate for 200 min at 1 atm pressure. The selection of the absorption time for 200 min would be suitable for most of the compounds to reach the equilibrium. The amine concentration in the solution could vary with the type of compound only to, e.g. molecular weight and solubility. As default MEA was chosen with a concentration of 2.5 mol/l.

The MEA concentration was chosen to be 2.5 mol/l. This concentration was selected in order to be able to compare as many compounds as possible at identical concentrations. It must be noted that by varying the molecular structure the corresponding molecular weight also changes and therefore it could turn to be impossible to compare, e.g. 50 wt.% solution of MEA and 5-amino-1-pentanol, respectively. Basically all the absorbents tested have a good solubility in water, except few compounds, e.g. hexylamine. Also varying the structure, the molecular weight of absorbents is altered. Therefore, it is not possible to carry out experiments with solvents that have always the concentration of 2.5 mol/l.

This must be regarded as a drawback of the present screening technique. Differences in concentration have effects on both the initial absorption rate and the total capacity, respectively. This can be seen in Fig. 2, in which the influence of the MEA concentration is presented on the equilibrium pressure of CO_2 at constant loading. However in this research the main focus is still at a level of different chemical species as to their reactive properties for CO_2 absorption. Therefore the present technique will be used for the first screening of various absorbents. The optimal operational concentrations for these absorbents are not yet known. All chemicals investigated (see Tables 1–3) were purchased from Sigma Aldrich Chemical Co.

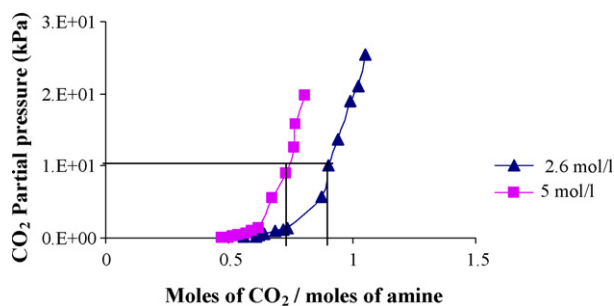


Fig. 2 – Solubility of CO_2 in 2.6 and 5.0 mol/l MEA aqueous solution at 40°C (Shen, K.-P., et al., 1992).

Table 1 – Total capacity of aqueous alkanolamine based absorbents: A (mol CO_2 /mol amine) and B (mol CO_2 /kg a-mine)

Aqueous absorbent	CO_2 loading	
	A	B
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{OH}$ Monoethanolamine	0.72	11.76
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$ 3-Amino-1-propanol	0.88	11.63
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$ 4-Amino-1-butanol	0.83	9.44
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$ 5-Amino-1-pentanol	0.84	8.05

Table 2 – Total capacity of aqueous alkylamine based absorbents: A (mol CO₂/mol amine) and B (mol CO₂/kg amine)

Aqueous absorbent	CO ₂ loading	
	A	B
$\text{H}_2\text{N}-\text{CH}_2\text{CH}_3$ Ethylamine	0.91	20.10
$\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{CH}_3$ Propylamine	0.77	12.96
$\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ Butylamine	0.86	11.74
$\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ N-Pentylamine	0.72	8.20
$\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ Hexylamine	1.52	15.05

Table 3 – Total capacity of aqueous diamine based absorbents: A (mol CO₂/mol amine) and B (mol CO₂/kg amine)

Aqueous absorbent	CO ₂ loading	
	A	B
$\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{NH}_2$ Ethylenediamine	1.08	17.93
$\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ 1,3-Diamino propane	1.30	17.66
$\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ 1,4-Diaminobutane	1.26	14.29
$\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ Hexamethylenediamine	1.48	12.71
$\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ 1,7-Diaminoheptane	1.34	10.28

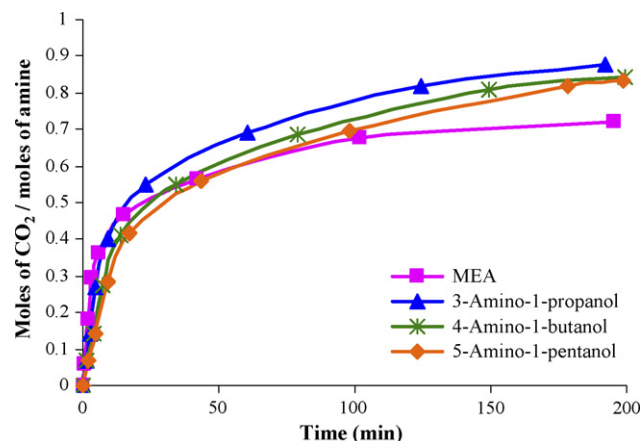
3. Results and discussion

Examination of the absorption from a pure CO₂ atmosphere, where saturation was reached for basically all absorbents within the experimental time frame, allows for a comparison of the absorption rates and saturation values. From the initial absorption rate an indication can be obtained about the reactivity of various amine based absorbents. It must be noticed, however, that due to the mass transfer effects, e.g. interfacial area and enhancement factor, that are contactor specific, no quantitative conclusions can be presented on the intrinsic kinetics between CO₂ and the amine used. However, the stirring speed of the absorbents was same, so differences would arise mainly due to the variations in physical properties, like, e.g. interfacial tension, density, viscosity and heat of absorption, these are characteristics for each compound.

3.1. Effect of chain length in alkanolamine

In Figs. 3–5, the effect of an increase in the chain length between the amine and hydroxyl group on the absorption rate and capacity of an alkanolamine based absorbents is shown. In these experiments the chain length varied from two carbon chain (MEA) up to five (5-amino-1-pentanol), respectively.

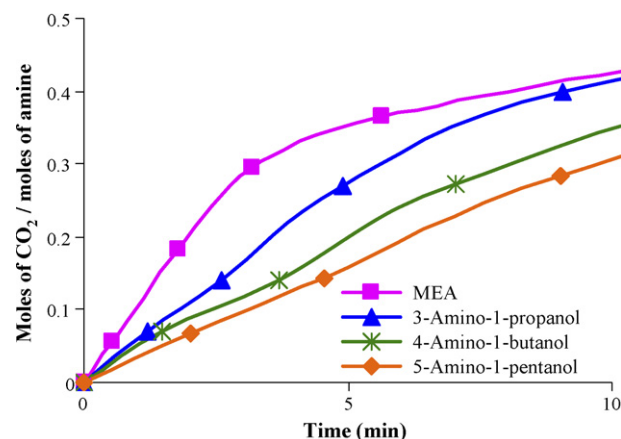
In Fig. 3, the overall results are presented. It must be noticed that the concentration of all alkanolamine was kept to 2.5 mol/l. MEA absorption capacity from these experiments is found to be 0.72 mol CO₂/mol amine, that is in good agreement with the results presented by Hook, R.J. (1997) for 2.5 mol/l aqueous MEA at 22 ± 0.5 °C, absorption capacity

**Fig. 3 – Influence of the chain length in alkanolamine for the absorption of CO₂ in aqueous absorbents.**

is 0.76 mol CO₂/mol amine, presented in his article. Increase in the chain length resulted in a slight increase in CO₂ absorption capacity till three carbon chain length 0.72–0.88 mol CO₂/mol amine (see Table 1 and Fig. 4). Further increase in chain length did not increase the absorption capacity, as it remains approximately the same.

Fig. 5 and Table 1 show the total capacity of CO₂ absorption for various alkanolamine in moles of CO₂/kg of amine. By comparing the results also in the unit of CO₂ absorbed per kilogram of amine will not even gives a better comparison of the absorbent also helps to understand the absorbent characteristic from the industrial point of view. Results show that the absorption capacity is decreasing from 11.76 to 8.05 mol CO₂/kg amine with increase in chain length. This could be caused by increase in molecular weight which means less moles of absorbent are present in the solution.

The effect of chain length on the initial absorption rate for alkanolamine is clearly shown in Fig. 4. Results show that increase of the chain length decreases the initial absorption rate in alkanolamine solution. The decrease in absorption rate

**Fig. 4 – Influence of the chain length in alkanolamine initial absorption rate for the absorption of CO₂ in aqueous absorbents.**

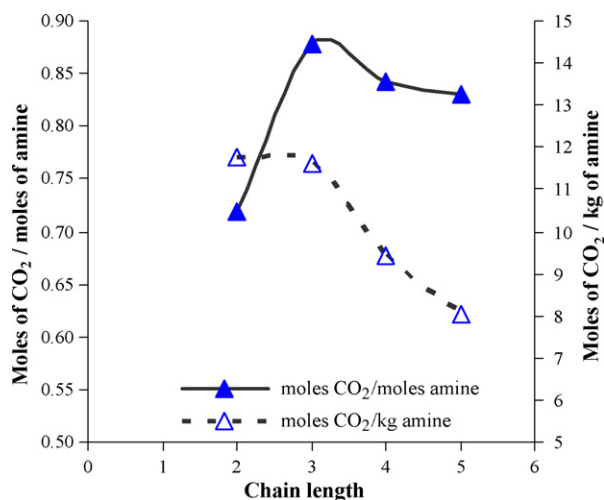


Fig. 5 – Influence of chain on the total absorption capacity of CO₂ in alkanolamine absorbents.

might be due to the fact that the formation of carbamate is slower. At this stage no further qualitative analysis will be presented on the initial absorption rate. As the absorption rate is a complex interaction between mass transfer, kinetics and equilibrium. The interpretation is not as straight forward as was expected before hand. Hence, overall in alkanolamine the absorption capacity in moles CO₂/kg amine and initial rate is decreasing with increasing in chain length. Where as the absorption capacity compared in the moles of CO₂/moles of amine is increasing slightly with increase in chain length.

3.2. Effect of chain length in alkylamines

In alkylamine experiments the chain length varied from two carbon chain (ethylamine) up to six (hexylamine), respectively. In Fig. 6, the overall results are presented. It must be noticed that the concentration of alkylamine up to five carbon chain (N-pentylamine) was kept at 2.5 mol/l. Due to the low

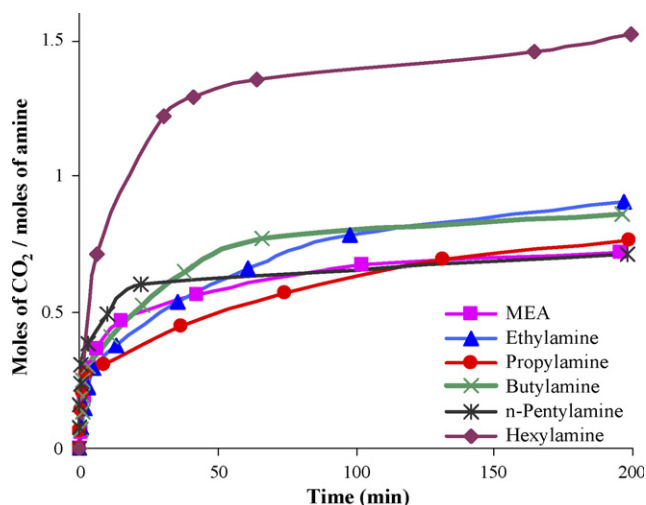


Fig. 6 – Influence of the chain length in alkylamine for the absorption of CO₂ in aqueous absorbents.

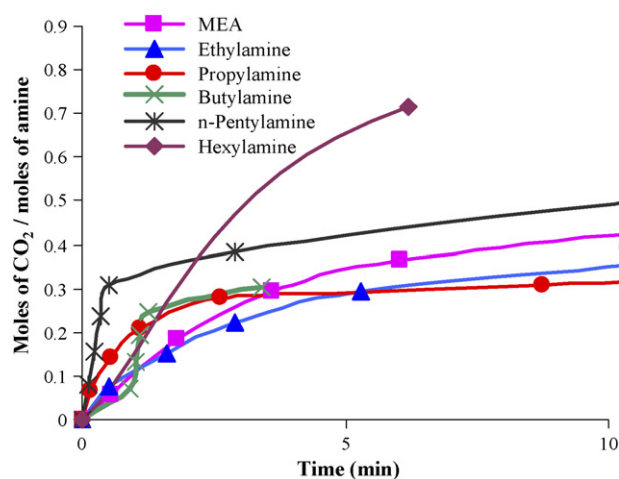


Fig. 7 – Influence of the chain length in alkylamine initial absorption rate for the absorption of CO₂ in aqueous absorbents.

solubility in water the concentration of six carbon chain (hexylamine) was only 0.1 mol/l. The influence of the chain length in alkylamines is shown in Figs. 6–8 and Table 2. Results from Figs. 6 and 8 and Table 2 show that increase in chain length from two carbon chain (ethylamine) to three carbon chain (propylamine) the CO₂ absorption capacity slightly decreases from 0.91 to 0.77 mol CO₂/mol amine. Further increase in chain length up to four carbon chain (butylamine) the CO₂ absorption capacity increases up to 0.86 mol CO₂/mol amine. Even though five carbon chain length (N-pentylamine) absorption capacity is decreased up to 0.72 mol CO₂/mol amine.

Interestingly, the six carbon chain (hexylamine) was found to have very fast absorption rate and high capacity, reaches up to 1.52 mol CO₂/mol amine. There can be two possible explanations for this behaviour, either the stability of hexylamine carbamate is very low, or there is hardly any formation of the carbamate in the solution, results into a higher amount of free amine in the solution available to react with CO₂. Fig. 7 shows that initial absorption rate in alkyl amines increases gradually with increase in chain length up to five carbon chain length, i.e. N-pentylamine.

Further increase in chain length reduces the initial absorption rate, e.g. in hexylamine. Hence, N-pentylamine might be an interesting absorbent on the basis of highest CO₂ initial absorption rate.

Increase in the chain length increases the molecular weight. Hence, comparing the moles of CO₂ absorbed per kilogram of amine in Fig. 8 shows that the ethylamine has the highest CO₂ concentration of 20.10 mol CO₂/kg amine (see Table 2) due to the lowest molecular weight. The absorption capacity decreases with increase in chain length up to five carbon chain (N-pentylamine) 8.20 mol CO₂/kg amine. Interestingly, the six carbon chain length (hexylamine), having higher molecular weight, still the CO₂ concentration increases up to 15.05 mol CO₂/kg amine. In addition, hexylamine has moderate carbamate stability resulting in increased absorbed amount of CO₂ when compared with N-pentylamine.

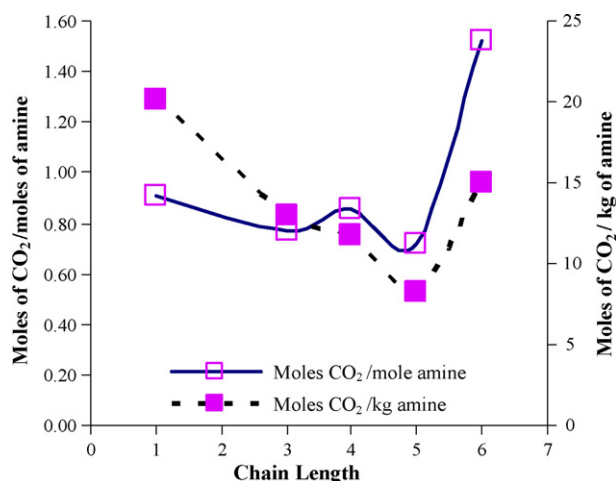


Fig. 8 – Influence of the chain length on the total absorption capacity in alkylamine for CO₂ absorption.

3.3. Effect of chain length in diamines

In the diamine experiments the chain length varied from two carbon chain (ethylenediamine) up to seven (1,7-diaminoheptane), respectively. In Fig. 9, the overall results are presented. It must be noticed that the concentration of diamine up to six carbon chain (hexamethylenediamine) was kept to 2.5 mol/l. Due to the low solubility in water the concentration of seven carbon chain (1,7-diaminoheptane) was kept at 1.5 mol/l. An increase in the chain length in diamines results in an increase of their absorption rate and capacity from 1.08 to 1.48 mol CO₂/mol diamine (see Figs. 9–11 and Table 3). This might very well be caused by the decrease in stability of the carbamate with increase in the chain length between the amine groups. Therefore, the number of free amine is higher and hence, the absorption capacity of these absorbents increases. Figs. 9 and 10 show that increase in chain length decreases initial absorption rate in diamines up

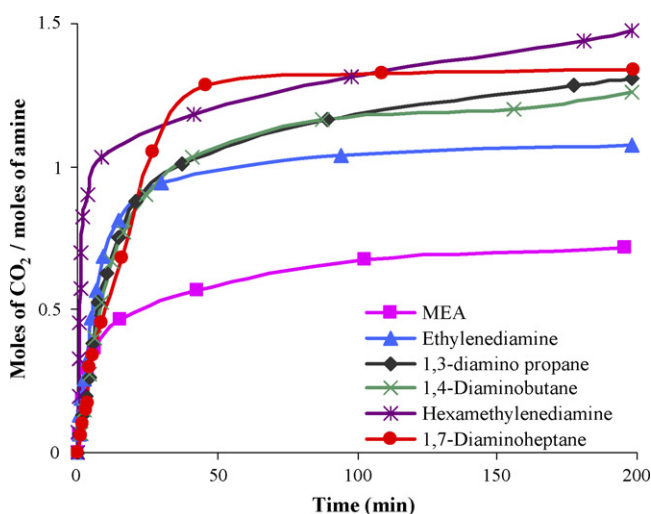


Fig. 9 – Influence of the chain length in diamine for the absorption of CO₂ in aqueous absorbents.

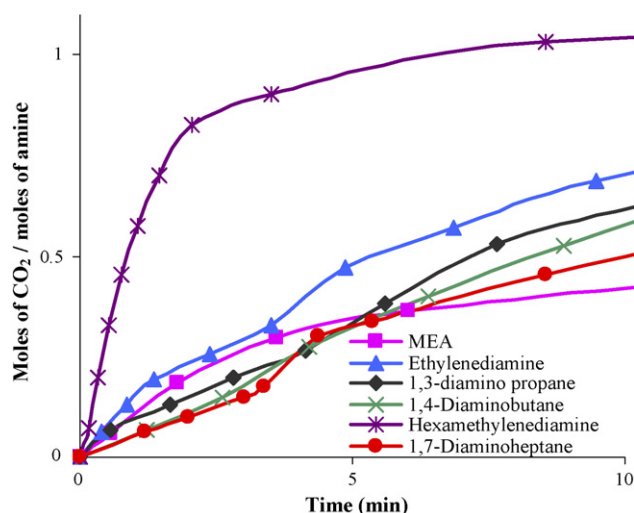


Fig. 10 – Influence of the chain length in diamine initial absorption rate for the absorption of CO₂ in aqueous absorbents.

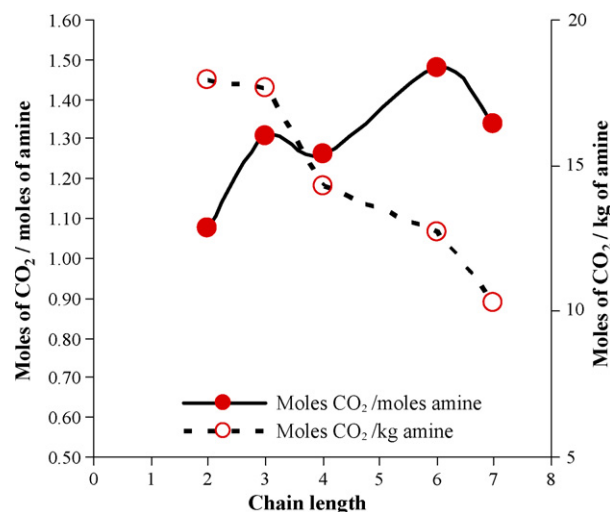


Fig. 11 – Influence of the chain length in diamine total loading for CO₂ absorption.

to four carbon chain length (1,4-diaminobutane). However, further increase in chain length up to six carbon (hexamethylenediamine), an exceptional increase in initial absorption rate was noticeable. Still when carbon chain length is increased up to seven (1,7-diaminoheptane), there is a tremendous decrease in the initial absorption rate.

From Fig. 11 and Table 3, it can be noticed that in diamine the absorption capacity remains in the same range up to four carbon chain length absorbent (1,4-diaminobutane) from 1.08 till 1.30 mol CO₂/mol amine. The absorption capacity of six carbon chain length (hexamethylenediamine) reaches up to 1.48 mol CO₂/mol amine (see Table 3 and Fig. 11). This might very well be caused by a formation of a hydrogen bond between the amine groups in this absorbent, thus creating a ring shaped structure. The hexamethylenediamine absorption properties are comparable with cyclic amines such as

piperazine. Upon a further increase in the chain length up to seven carbon (1,7-diaminoheptane), the capacity decreases up to 1.34 mol CO₂/mol amine. Hence, hexadimethylenediamine is the most interesting absorbents in diamines based on high initial absorption rate and capacity.

Fig. 11 also shows the comparison of diamines absorption capacities in mol CO₂/kg amine. With an increase in the chain length, the CO₂ absorption capacity is decreasing per kilogram of diamines that could be caused by the increase in molecular weight. Ethylenediamine has the highest absorption capacity for CO₂ up to 17.93 mol CO₂/kg amine. However, from these results ethylenediamine and hexadimethylenediamine could thus have a greater potential for CO₂ absorption.

Interestingly when comparing the behaviour of alkylamine and diamine absorption capacities on the basis of moles of CO₂ per kilogram of amine (see Figs. 8 and 11), it can be noticed that in alkylamines the CO₂ absorption capacity increases with six carbon chain, whereas in diamines the absorption capacity decreases gradually with increase in the chain length. This is due to the reason that alkyl amines are lighter in molar weight than that of diamine. Therefore, from these results it is clear that the structural effect is very important in the behaviour amine based absorbents for CO₂ absorption.

4. Conclusions

The present study revealed some of the structural effects of various amine based aqueous solvents on their initial CO₂ absorption rate and capacities. An increase in the chain length in alkylamines resulted in a decrease in the initial absorption rate, whereas the capacity increased in most cases. An exceptional increase in the absorption rate and capacity was noticed with six carbon chain length amine based absorbents (hexadimethylenediamine and hexylamine). Alkyl

and amine group were most suitable substituted functional groups in order to enhance the absorption rate and capacity of amine based absorbents. Whereas, substitution of hydroxyl group decreases the initial absorption rate and increases the capacity. This study will be advantageous in the development of an improved amine based CO₂ absorbent, lead to a better approach for development of new technologies in the CO₂ capture area.

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